Advanced DoD QSM for Chemists

26 March 2007

Welcome

- Instructors
- Logistics
- Detailed Question Parking Lot
- Opening Activity

Opening Activity

- Quick Questions To Determine Your Level of Familiarity With the DoD QSM

Agenda

- DoD QSM Review
- DoD Assessment Philosophy & Frequent Findings
- Review of Common Technical Questions & Issues
- Wrap Up

DoD QSM Review

Review of the DoD QSM

- What Is the DoD QSM?
- How Was the DoD QSM Developed?
- Who Needs To Use the DoD QSM?
- Why Do I Have To Use the DoD QSM?
- Most Important “Themes” of the DoD QSM
- Project-specific Requirements or “Variances”
- DoD Assessment Philosophy & Frequent Findings

What Is the DoD QSM?

- Department of Defense Quality Systems Manual (QSM) for Environmental Laboratories, Version 3.0, January 2006
  - Set of requirements and guidance to establish and manage quality systems for environmental testing laboratories that work for DoD
  - ***Baseline*** set of requirements
  - Gray boxes
    - Clarifications
    - Additional DoD requirements

How Was the DoD QSM Developed?

- ISO/IEC 17025 Requirements (General Testing and Calibration Laboratory Requirements)
- NELAC Chapter 5, 2003 Version, Quality Systems Requirements (Environmental Laboratory Requirements)
- DoD QSM Gray Boxes
  - Additional DoD requirements
    - USACE Shell
    - AFCEE QAPP
    - Navy IR documents
  - NELAC Standard & SW-846 Method Clarifications
  - Good laboratory practices

Who Needs To Use the DoD QSM?

- Public (i.e., Government) and Private Laboratories, Contracted With DoD Either:
  - Directly
  - Through a prime contractor, subcontractor, or A-E Firm
- DoD Contracting Personnel, Who Will Use the DoD QSM To Ensure Consistency With DoD QSM When Drafting Contracts
- DoD Oversight Personnel and Assessors, Who Use the DoD QSM to Uniformly and Consistently Evaluate the Laboratory's Implementation of DoD QSM

Why Do I Have To Use the DoD QSM?

- DoD Instruction 4715.15 – Environmental Quality Systems Issued 11 December 2006
- Reduce Redundancy and Inconsistency Among the Three Services
- DoD QSM Does Not Relieve a Laboratory from Complying With:
  - Contract requirements
  - Host-nation governing standards
  - Federal, state, or local regulations

Most Important “Themes” of the DoD QSM

- Quality Systems Elements – Management
  - Quality system, project coordination, internal audits, ethics training
- Sample Handling
  - Sample handling, subcontracting of environmental tests
- Quality Systems Elements – Technical
  - Personnel, environment, equipment, calibration, standards & reagents, methods & SOPs, QC, PT
- Data Management
  - Record keeping, reporting, data and records

Project-Specific Requirements or “Variances”

- ***No*** Variances Permitted for the DoD QSM
  - ***Baseline*** set of requirements for laboratories
- Project-specific Requirements
  - Variances are permitted
  - Must be approved and documented
- Hierarchy of Requirements
  - Laboratory assessments for DoD QSM compliance
    - DoD QSM, reference methods, project-specific
  - Project execution
    - Project-specific, DoD QSM, reference methods

DoD Assessment Philosophy & Frequent Findings

DoD Assessment Philosophy

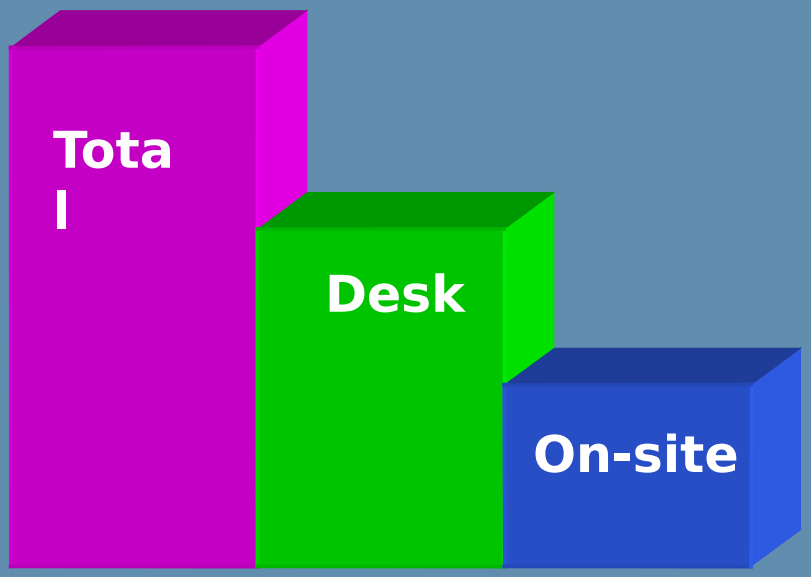
- Assessments Can Be For:
  - Pre-qualification
  - Project-specific needs
  - Continuing biannual laboratory compliance
- Moving Towards More Project-Specific Assessments
- On-site Assessment May Be Required
  - If no on-site assessment based on NELAC Standard or DoD QSM during past 2 years
  - If had an on-site assessment with significant findings
  - If significant findings were found during desk assessment every 2 years

DoD Assessment Philosophy
(continued)

- Stresses Review of Documentation and Previous Assessments
  - Recent NELAP, DoD, or other accreditations
  - PT results, LOD, and LCS results
  - SOPs and quality manual
  - Check repeat deficiencies from previous assessments
- Takes into Consideration
  - Scope of work
  - Quality of laboratory's documentation
  - Quality of laboratory's past performance

2006 Assessments

- 42 Assessments
  - 29 desk assessments
  - 13 on-site assessments



2006 DoD Frequent Findings

- Laboratory Procedures for Determining MDL, LOD, LOQ, and Reporting Limits Do Not Meet DoD Requirements
- Initial Calibration Frequency, Acceptance Criteria, and Documentation Do Not Meet DoD QSM Requirements
- Not all SOPs Relevant to DoD Work and/or Quality Manual Have Been Reviewed in the Last Year
- Laboratory Procedures for Establishing and Verifying Retention Time Windows Do Not Meet DoD QSM Requirements
- Method Blank Acceptance Criteria Do Not Meet DoD QSM Requirements

2006 DoD Frequent Findings
(continued)

- In-house QC Acceptance Limits for MS Recovery Exceed that of the DoD QSM
- Continuing Calibration Verification Frequency, Acceptance Criteria, and Documentation Do Not Meet DoD QSM Requirements
- SOPs Lack Sufficient Detail
- In-house QC Acceptance Limits for LCS Recovery Exceed that of the DoD QSM
- In-house RPD Acceptance Limits for MS/MSD Exceed that of the DoD QSM

Review of Common Questions & Issues

Quality Systems Management

- Annual Document Review
  - SOPs & Quality Manual must be reviewed annually
  - DoD QSM Box 32
- Detailed Documentation To Allow for Reconstructed Results – e.g., When Manual Integrations Are Performed Records Must Include:
  - Complete audit trail
  - Raw data output showing results (before & after)
  - Notation of rationale, date, & signature/initials
  - DoD QSM Section 4.12 & Box 50
- Ethics & Data Integrity Training
  - Annually & as part of new employee training
  - DoD QSM Section 5.2.7

Methods and SOPs

- SOPs as Stand Alone Instructions
  - Laboratories shall maintain SOPs that accurately reflect all phases of current laboratory activities, such as:
    - Assessing data integrity
    - Corrective actions
    - QA/QC procedures (e.g., control charts)
    - All test methods
  - DoD QSM Section 5.4.1.1
- Poor Performing Analytes
  - Extraction issues
  - Instrumentation issues
  - DoD QSM Appendix DoD-D Section D.5

Equipment

- Preservation of Samples – Thermal
  - Temperature measurement
    - Must monitor 7 days a week
    - Low-cost devices can be used to validate that proper temperature is continuously maintained
      - With memory
      - Circle chart thermometers
  - DoD QSM Box 68

Sample Preparation

- Matrix Spike & Surrogates Must Be Added to Samples Prior to Any Processing Steps (e.g., pH Adjustment, Adding Drying Agents, etc.)
  - Section 8.3.1 of Method 3500C
- Subsampling Technique
  - No weight targeting to a narrow range for metals in soils
  - Method 8330B – Follow Appendix A.5.0
  - Pierre Gy's Sampling Theory & Sampling Practice
  - ASTM Standard D 6323

Initial Calibration

- Initial Calibration Range
  - Organics: minimum of 5 contiguous calibration points
  - Inorganics: minimum of 3 contiguous calibration points plus a calibration blank, except for ICP (Minimum of 1 high standard and 1 calibration blank)
- All Reported Target Analytes and Surrogates Included
- For Multicomponent Analytes, Such as PCBs, Toxaphene, and Technical Chlordane, Separate Initial Calibrations Are Required

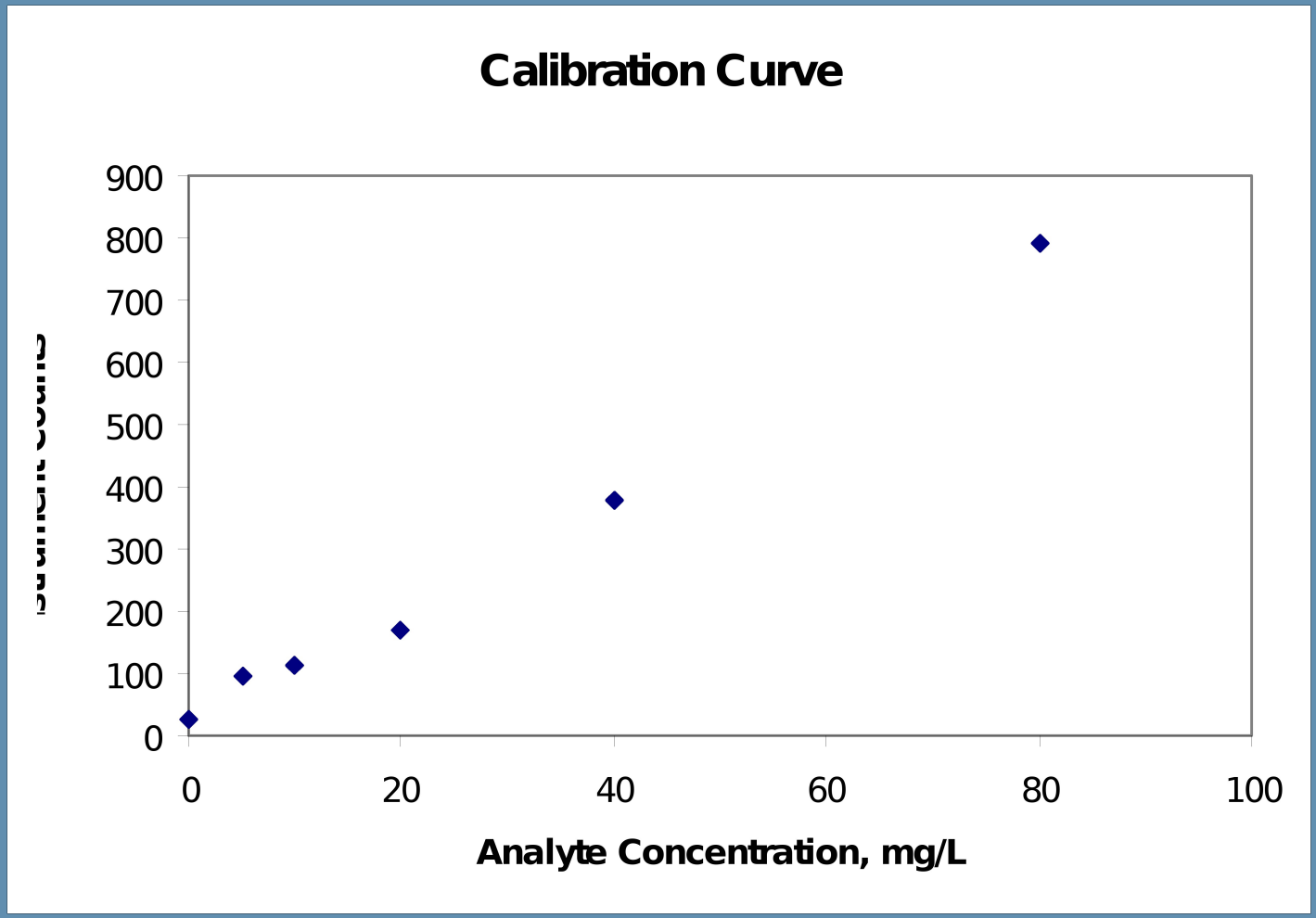
Initial Calibration (continued)

- Initial Calibration Frequency, Acceptance Criteria, and Documentation Must Meet DoD QSM Requirements
- “No Grand Mean” Technique for the GC/MS Methods
- For Regression Analyses
  - No blank correction
  - No force through origin

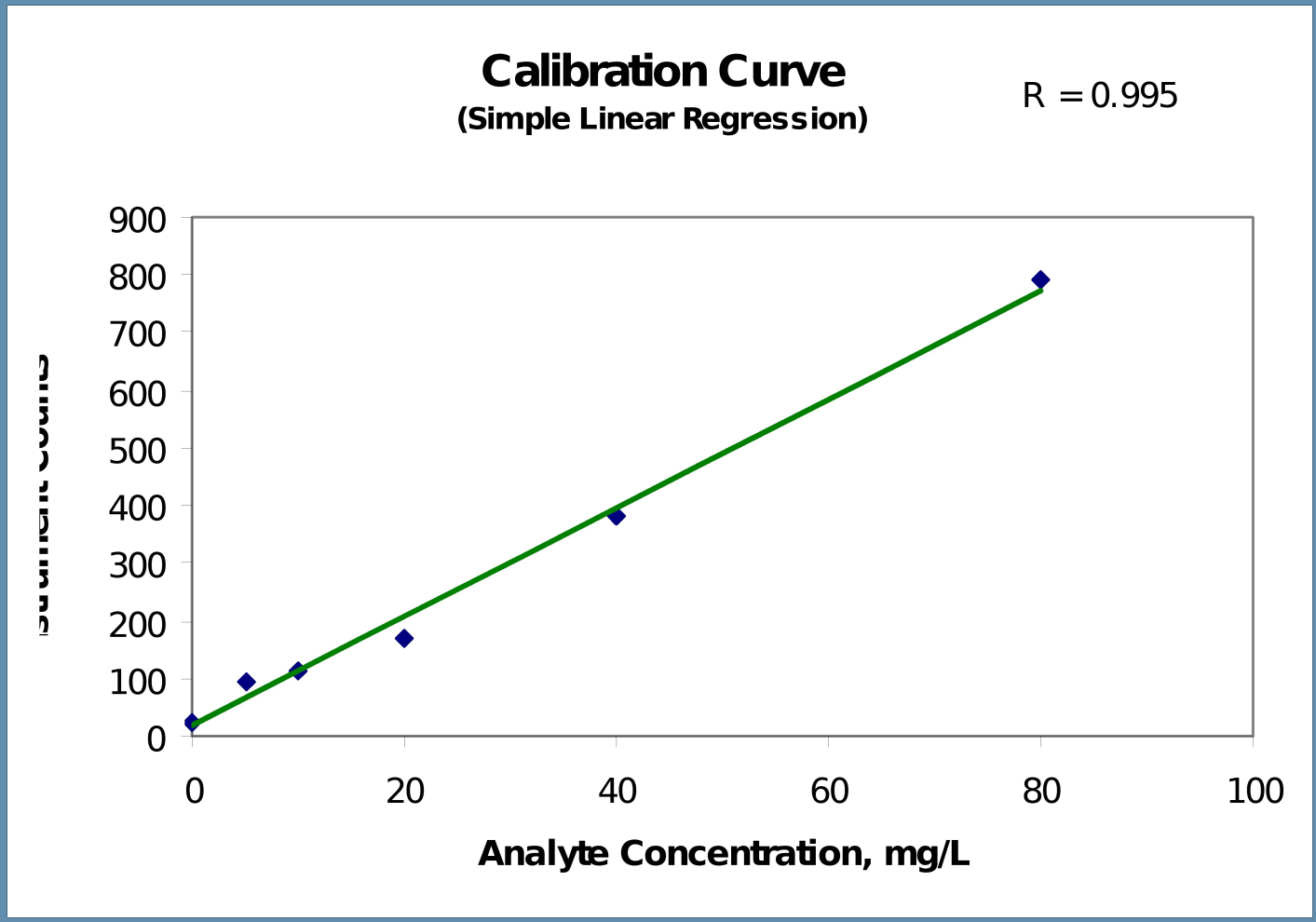
Force Through Origin

- Found in Many Assessments During 2006
- Used in Initial Calibration for the Following:
  - Anions
  - VOCs
  - Trace Metals
  - Wet Chemistry
- Most Software Packages Have Force Through Origin as an Option
  - DoD Discourages this Practice

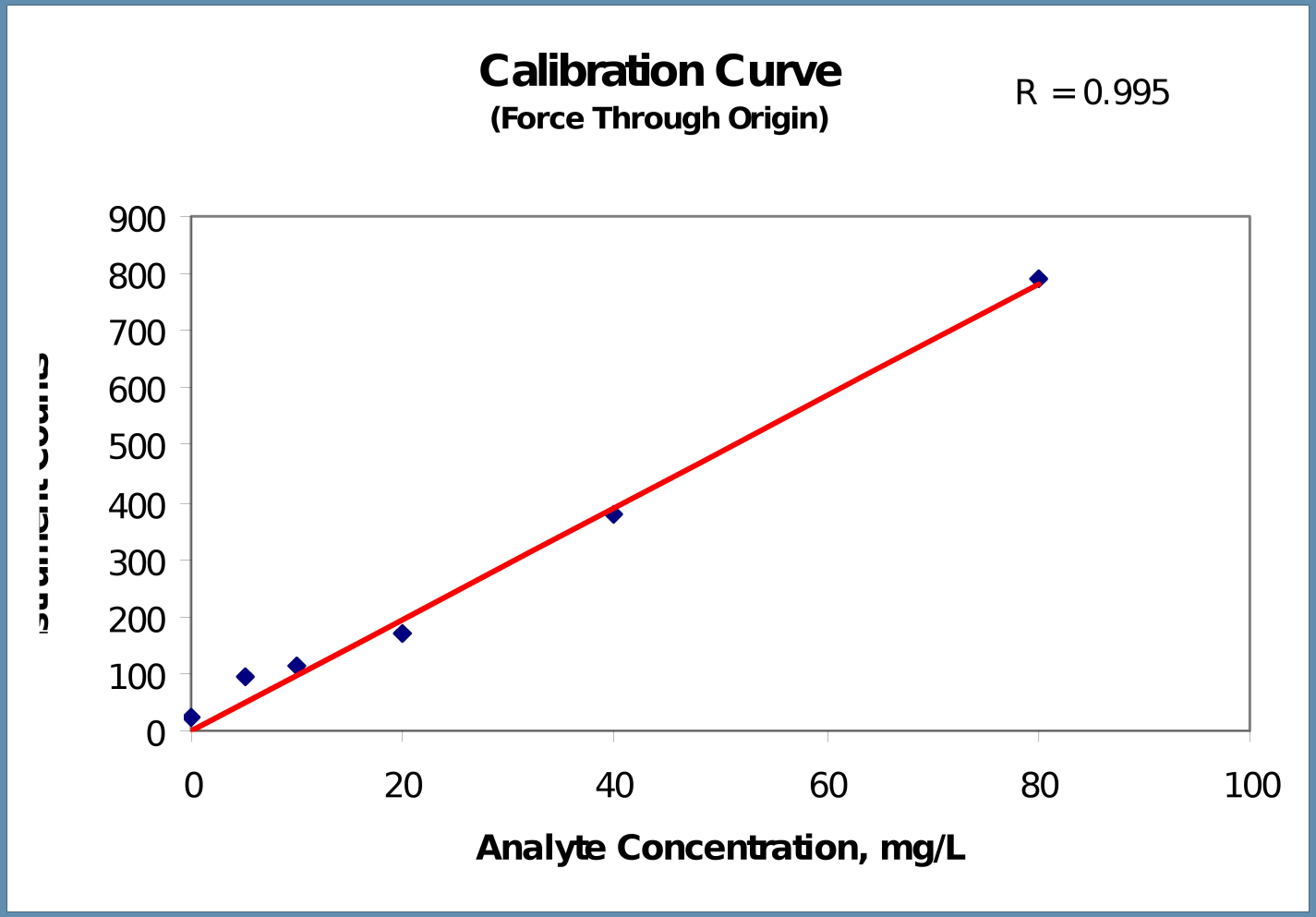
Calibration Curve



Simple Linear Regression

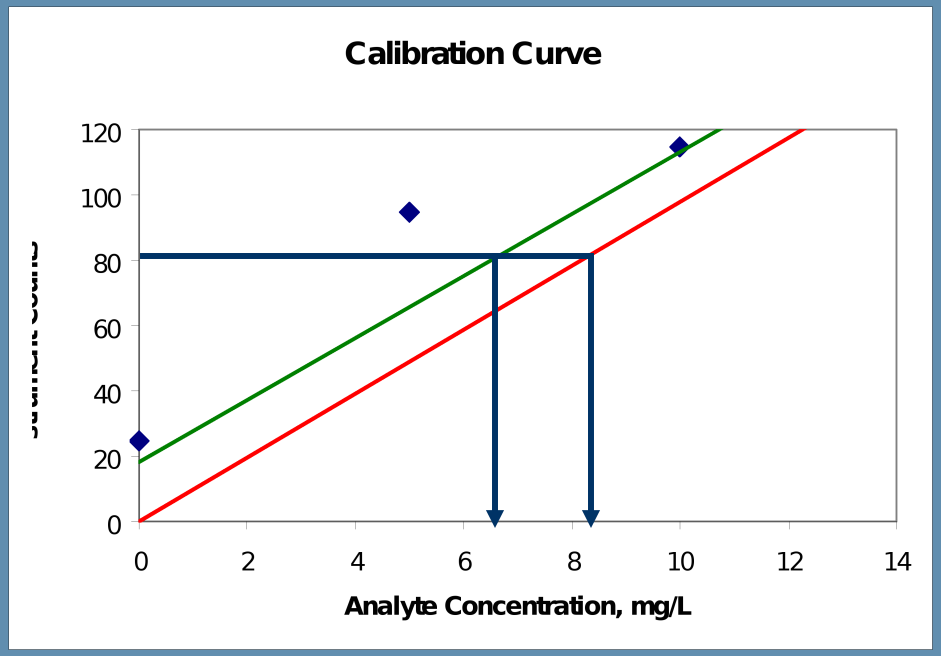


Force Through Origin



Simple Linear Regression v. Force Through Origin

- Both Simple Linear Regression and Force Through Origin Pass Calibration Criteria of ≥ 0.995 Correlation Coefficient (r)
- However, at the Low End of the Curve Force Through Origin, in This Example, Is Approximately 25% Greater Than Simple Linear Regression



Break

10 Minute Break – Please Be Back in 10 Minutes

Second Source Calibration Verification

- Minimum Frequency, Acceptance Criteria, and Documentation Need To Meet DoD QSM Requirements
  - GC/HPLC
    - Frequency – once immediately after initial calibration
    - Acceptance criteria – value of second source for all analytes within ± 20% of expected value (initial source)
    - DoD QSM Appendix DoD-B: Table B-2
  - GC/MS
    - Frequency – once immediately after initial calibration
    - Acceptance criteria – value of second source for all analytes within ± 25% of expected value (initial source)
    - DoD QSM Appendix DoD-B: Table B-3

Continuing Calibration Verification (CCV)

- CCV Minimum Frequency, Acceptance Criteria, and Documentation Must Meet DoD QSM Requirements
  - Continuing calibration frequency – after every 10 field samples and at the end of the analysis sequence
  - Acceptance criteria – all analytes within ±20% of expected value
  - Corrective actions for CCV

Retention Time (RT)

- Procedure for Establishing and Verifying RT Windows for Each Analyte & Surrogate
- GC/HPLC
  - RT position
    - Established once per ICAL & at the beginning of an analytical shift
    - Set using the midpoint standard of the ICAL or the CCV run at the beginning of an analytical shift
  - RT width
    - Calculated at method set-up and after major maintenance (e.g., column change)
    - ± 3 times standard deviation for each analyte RT from 72-hour study or 0.03 min, whichever is greater
  - RT verification after each CCV
  - Appendix DoD-B: Table B-2

Retention Time (RT) (continued)

- GC/MS
  - RT window
    - Established once per ICAL
    - Position set at the midpoint standard of the ICAL or the CCV run at the beginning of an analytical shift
  - RRT for each analyte in each calibration standard within ± 0.06 RRT units
  - Appendix DoD-B: Table B-3
- IC
  - RT position
    - Established once per ICAL at midpoint of ICAL
  - RT width
    - Calculated at method set-up and after major maintenance
    - ± 3 times standard deviation for each analyte RT over 24-hour period
  - RT verification after each CCV
  - Appendix DoD-B: Table B-10

Method Detection Limit

- The Minimum Concentration of a Substance That Can Be Measured and Reported With 99% Confidence That the Analyte Concentration Is Greater Than Zero
- Required for Each Analyte (Including Surrogates) and Matrix
- Requirements Established in 40 CFR 136B Are the Baseline (or Minimum) Source of Information for Determining MDLs

Method Detection Limit
(continued)

- MDLs Determined Using Minimum of 7 Replicates
  - Appropriateness of the spiked concentration evaluated based on the ratio between the mean recovered concentration and the calculated MDL should be within
    - 1 – 5 for reagent water matrix
    - 1 – 10 for other matrices
  - For Multi-Analyte Analyses the Ratio of the Majority (e.g., 2/3) Analytes Should Meet
- Other Published Statistical Methods May Be Appropriate as Supplemental Resources in Determining MDLs , if an Analyte Can Be Reliably Detected at 99% Confidence

MDL Verification Check

- MDL Verification Shall Be Performed After Each MDL Study
- Low-level Spike at Approximately 2 Times the Calculated MDL
  - Taken through preparatory and analytical steps
  - Used to verify that the laboratory can detect analytes at the calculated MDL
  - Acceptable if reliably detected & identified by method-specific criteria (S/N ≥3, analytes ID confirmed)
- If the MDL Verification Fails
  - Calculated MDL may be biased low
  - Reprep and reanalyze MDL verification check at a higher level to set a higher MDL or the MDL study must be repeated

An Example of Good Science

- Variance Calculation for Standard Deviation
- IDLs
  - Typically, laboratories average the standard deviations of 7 replicates from 3 non-consecutive days
  - Standard deviations can not be summed
- Standard Deviation

$$\sigma_{pooled} \neq (\sigma_1 + \sigma_2 + \sigma_3) / 3$$

$$\sigma_{pooled} = \sqrt{\frac{(n_1 - 1) \times \sigma_1^2 + (n_2 - 1) \times \sigma_2^2 + (n_3 - 1) \times \sigma_3^2}{(n_1 - 1) + (n_2 - 1) + (n_3 - 1)}}$$

Quantitation Range

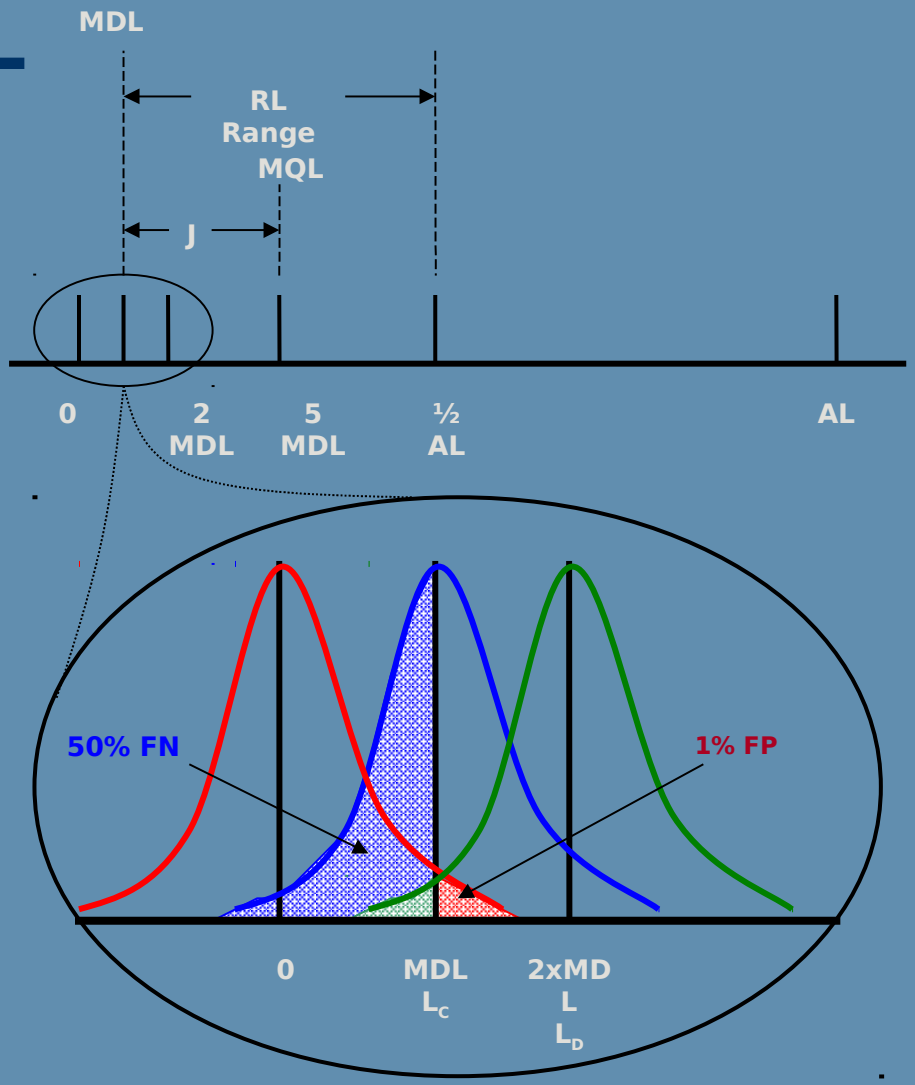
- Quantitation Range Is Defined by the Low and High Calibration Standards of the Initial Calibration Curve (or the Low-level Calibration Check Standard for Methods That Allow Only One Standard)
- Method Quantitation Limit (MQL) – Set at a Factor 5 –10 Times the MDL for Most Target Analytes in a Method, but No Lower Than Three Times the MDL for Any Single Target Analyte
- LOQ Must Be at Least Three Times the LOD, S/N ≥ 10

Activity

Define RL

1. RL = MQL, Below it J-flag Data
2. RL ≥ Lowest Calibration Standard
3. RL = Project Determined Limits for Reporting Non-detects
4. RL = Project-required Quantitation Limits That Must Be No Greater Than ½ Action Level

Relationships Between MDL (L_C), MDL Verification (L_D), MRL, RL, and AL



Break

10 Minute Break – Please Be Back in 10 Minutes

ICB/CCB and ICSA/ICSAB Acceptance Criteria

- ICB/CCB
  - ICB must be run at the beginning of an analytical run immediately after ICV
  - CCB
    - Must be run at the beginning of an analytical run, after every 10 samples and at the end of an analytical run
    - Must be run immediately after a CCV
  - No analyte in ICB/CCB may be detected at > 2x MDL in the ICB/CCB
- ICSA/ICSAB
  - ICSA/ICSAB must be run at the beginning of an analytical run
  - The absolute value of all nonspike analytes in ICSA must be < 2x MDL (unless they are a verified trace impurity from one of the spiked analytes)
  - ICSAB percent recovery must be within ± 20% of the expected value

Blank Acceptance Criteria

- No Analytes Detected > ½ RL
- No Common Laboratory Contaminants Detected > RL
- Reporting Limit (RL) – Defined By the Client
- If the Method Blank Fails, the Laboratory Shall Evaluate Whether Reprocessing/Reanalysis of the Associated Samples Are Necessary
  - Any sample associated with a failed method blank shall be reprocessed/reanalyzed, except for samples with no detection, in a subsequent preparation batch. Data should still be B-flagged
  - If no sample volume remains for reprocessing, the results shall be reported with B-flag
- Same Criteria Apply to TB and RB

LCS Study

- DoD EDQW: Development of DoD Laboratory Control Sample Control Limits, May 2004
  - Study initiated in 1999 – participation of ACIL, laboratories, EDQW & three DoD Services
  - Objectives
    - Develop & publish LCS control limits based on empirical data used by laboratories doing work for DoD
    - Establish objective benchmarks for analytical method performance to assist in evaluating the suitability of alternative methods
  - Study included data from multiple laboratories

LCS Control Limits

- How To Use DoD QSM LCS Limits
  - Minimum for laboratory performance, compared with in-house statistically derived limits for laboratory screening, default limits for batch QC if project-specific limits are not available, etc.
  - Laboratory must have control charts/control limits and SOP, establish its in-house statistically derived LCS control limits (LCS-CL), and include failed LCS for control limits study (failed LCS may be eliminated only if there is documented, scientific valid evidence)
  - A laboratory is not allowed to use DoD QSM limits if its statistically derived LCS control limits are not consistent with DoD QSM Limits
    - Need improved performance
    - Use a different method/laboratory

LCS Control Limits (continued)

- Marginal Exceedances (ME)
  - Defined as beyond the LCS-CL but still within the ME limits (set at 4 standard deviations around the mean)
  - Must be sporadic (i.e., random)
    - If the same analyte exceeds the LCS-CL repeatedly (e.g., 2 out of 3 consecutive LCS) – the problem is systematic and something is wrong with the analytical system
  - Table D-1 presents the allowable number of MEs, based on binomial statistics
- LCS Failures
  - Exceedance of a LCS-CL by any project-specific analyte of concern
  - MEs of the LCS-CLs by more than the allowable number of analytes
  - Exceedance of the ME limits by one or more analytes
- LCS Failures Require Corrective Action

LCS Control Limits (continued)

- Poor Performing Analytes
  - Defined as having a lower control limit of 10% or less
  - Include all target analytes in calibration standard including poor performing analytes
  - If a poor performing analyte is a project-specific analyte of concern or is detected in the project samples, contact the client to determine course of action. Either:
    - alternative method to test for the analyte
    - modify the original method to optimize conditions for the poor performing analyte
  - Will not be used to control batch acceptance

LCS Control Limits (continued)

- In-house Limits
  - Utilized as part of quality control system – evaluate trends and monitor and improve performance
  - When outside DoD control limits (upper &/or lower)
    - Contact Client for corrective actions
    - Report in-house limits in laboratory report even if the LCS associated with the batch fell within the DoD limits
  - When within DoD control limits
    - Use in-house limits for QC monitoring
    - May report data using DoD limits
- DoD Control Limits Not Available
  - Use DoD limits for similar methods
  - Use method specified performance data
  - Use in-house limits

Matrix Spike/Matrix Spike Duplicates (MS/MSD)

- Each Preparatory Batch of DoD Samples Must Contain an Associated MS and MSD Using the Same Environmental Matrix Collected for the Specific DoD Project
- Matrix Spike
  - MS shall contain all project-specific target analytes
  - MS recovery shall be compared with LCS recovery limits
  - MS concentration shall be 1 – 4 times of sample concentration (CLP's inorganic NFGs is not acceptable)
  - RPD calculation shall be based on concentration, not % R
- Laboratories In-house QC Acceptance Limits for MS Recovery Exceed That of the DoD QSM

Matrix Spike/Matrix Spike Duplicates (MS/MSD) (continued)

- GC/HPLC and GC/MS Matrix Spike Duplicate or Sample Duplicate – Acceptance Limits
  - RPD ≤ 30% (between MS & MSD or sample & sample duplicate)
  - Appendix DoD-B: Table B-2 and B-3
- Common Anions Matrix Spike Duplicate – Acceptance Limits
  - RPD ≤ 20% (between MS and MSD)
  - Appendix DoD-B: Table B-10
- Colorimetric Hexavalent Chromium Matrix Spike Duplicate or Sample Duplicate – Acceptance Limits
  - Aqueous matrix: RPD ≤20% (between MS and MSD or sample and sample duplicate)
  - Solid matrix: RPD ≤30% (between MS and MSD or sample and sample duplicate)
  - Appendix DoD-B: Table B-8

Measurement Uncertainty

- Environmental Testing Laboratories Shall Have and Apply Procedures for Estimating Uncertainty of Measurements
- When Estimating the Uncertainty of Measurement, All Uncertainty Components Which Are of Importance in the Given Situation Shall Be Taken Into Account Using Appropriate Methods of Analysis
  - LCS control limits are minimum uncertainty
  - Nested approach
  - Any published or scientifically valid procedure
- Data of Unknown Quality Can Not Be Compared

Proficiency Testing (PT)

- PT Passing – How Is it Judged?
- PT Studies
  - High rate of unsatisfactory results found in the PT studies
  - PT studies were not performed or submitted for every approved matrix
  - Correction of problems through documentation of a successful PT study is not demonstrated
    - Need to investigate and resolve
    - Corrective action for any PT failure
    - May do a quick turn-around PT

Reporting

- Q-flag
  - One or more quality control criteria (e.g., LCS recovery, surrogate spike recovery, second column confirmation, etc.) failed
  - Data usability should be assessed by project team
  - Typically LIMS system needs to be modified
- Second Column Confirmation of Positive Results
  - Minimum frequency
  - Acceptance criteria
  - Flagging criteria

Additional Technical Questions from Participants

- What Questions Do You Have?

Wrap Up

Where To Go for More Help

- Web Sites
  - Copies of DoD QSM can be downloaded from:

    http://www.navylabs.navy.mil (NavyLabs web site)

    https://www.denix.osd.mil/denix/Public/Library/ Compliance/EDQW/admin.html (DENIX web site)
  - Frequently Asked Questions (FAQs) online at:

    http://www.navylabs.navy.mil/faq.htm
  - Example FAQs:
    - How do I use a Q-flag?
    - How do I report a second column confirmation?
    - When is it permissible to exclude calibration points?
    - What about linear dynamic ranges and dilutions?
    - When does hold time end?

Where to Go for More Help
(continued)

- EDQW Open Forum: Friday, March 30
  - An opportunity to discuss any and all issues related to DoD QSM Version 3
  - Answers to questions in the “Parking Lot”
- Additional Questions Can Be Sent to: lqao@navsea.navy.mil

Final Questions?

- Any Final Questions?
- Evaluation Form
  - Please fill out the evaluation form so that we may improve our training for next time